

**AMINE AND QUATERNARY AMMONIUM SALT DERIVATIVES
OF GLYCIDYL ETHERS AND GLYCIDYL ESTERS**

5 **I claim the benefit under Title 35, United States Code, § 120 to U.S. Provisional Application Number 60/281,899, filed April 5, 2001, entitled AMINE AND QUATERNARY AMMONIUM SALT DERIVATIVES OF GLYCIDYL ETHERS AND GLYCIDYL ESTERS**

BACKGROUND OF THE INVENTION

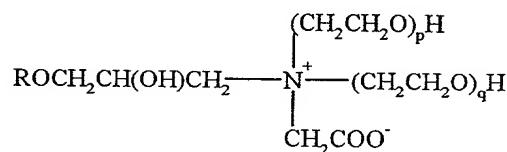
10 **1. Field of the Invention**

The present invention relates to the compounds of amine and quaternary ammonium salt derivatives of glycidyl ethers and glycidyl esters, preferably alkoxylated derivatives, which are useful in personal care, oil field, industrial and institutional cleaners, and agricultural formulations.

15 **2. Description of Related Art**

The reaction of alcohols with epichlorohydrin, which provides the intermediates for the compounds of the present invention, is known in the art.

20 U.K. Patent No. 1,164,095 discloses a method of preparing a photographic light-sensitive element by applying photographic coating compositions to a support, which method comprises incorporating in at least one coating composition before application a compound represented by the general formula:



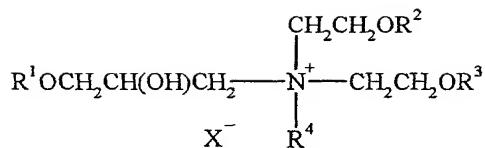
25 wherein R represents an alkyl group having 8-20 carbon atoms, and p and q each represents a positive integer.

U.S. Patent No. 3,932,495 discloses a process for preparing quaternary ammonium compounds which contain both cationic and nonionic hydrophilic groups in the molecule. Alkylene oxide is reacted with aliphatic alcohol in the presence of an alkali catalyst at an elevated temperature; the resulting alkoxyglycol alcohol or ether is reacted with 5 epichlorohydrin, producing the corresponding chloroglyceryl or chlorohydroxypropylene ether; and this is then reacted with a secondary amine to produce the quaternary ammonium compound.

U.S. Patent No. 4,145,307 discloses water-in-oil emulsifiers that are obtained by reacting fatty alcohols with epichlorohydrin and reacting the resulting glycidyl ethers with amines.

U.S. Patent No. 4,490,279 discloses foam stabilized compositions containing (a) a high foaming nonionic surfactant which is a block copolymer that is an alkylene oxide adduct of ethylene glycol, propylene glycol, or diethylene glycol, and (b) a foam-stabilizing amount of an amine oxide derived from a fatty alcohol which has been oxyethylated to the extent that 15 ethylene oxide units account for approximately 50 to 75 weight percent of the molecular weight of the fatty alcohol-ethylene oxide adduct. The compositions are said to be useful in the formulation of various products in which foam stability is needed, such as hand detergent bars, hair shampoos, rug shampoos, hand dishwashing detergents, etc.

U.S. Patent No. 6,176,906 B1 discloses a photo-curable antifogging composition 20 which may be applied to substrates such as glass, various plastic materials and the like to give antifogging property on the surface of these substrates. The main ingredient of the composition is a quaternary ammonium salt of the following formula (1):



wherein: R^1 is $\text{CH}_3(\text{CH}_2)_n\text{CH}_2$ or $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{C}_6\text{H}_4$ wherein n is an integer from 1 to 16 inclusive; R^2 and R^3 are the same or different from each other, and represent $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2$, $\text{CH}(\text{OH})\text{CH}_2$, $\text{CH}_2=\text{CHCOOCH}_2\text{CH}(\text{OH})\text{CH}_2$ or H , with the proviso that R^2 and R^3 may not be H at the same time; R^4 is H , CH_3 , CH_3CH_2 or $\text{CH}_3\text{CH}_2\text{CH}_2$; and X is CH_3OSO_3 , $\text{CH}_3\text{CH}_2\text{OSO}_3$, CH_3COO , CF_3COO , $\text{CH}_3(\text{CH}_2)_n\text{COO}$ wherein n is an integer from 1 to 16 inclusive, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)\text{COO}$, $\text{C}_6\text{H}_5\text{COO}$, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO}$, $\text{HOOCCH}_2\text{CH}(\text{OH})\text{COO}$, Cl or Br .

Polish Patent No. 139,477 discloses the preparation of



by reacting



15 with



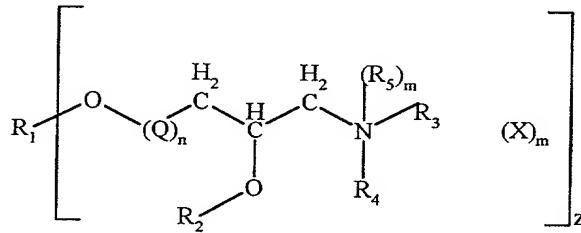
wherein R is C_{4-36} alkyl, C_{4-36} alkenyl; R_1 , R_2 are C_{1-4} alkyl, hydroxyalkyl, $(\text{CH}_2\text{CH}_2)_n\text{H}$, n is 1-16; Z is $\text{CH}=\text{CH}$, alkenyloxy, etc.; and R_4 is H , NH_4 , alkenyloxy, etc. The compounds thus produced are said to be useful as antistatic agents, microbiocides, and sequestering agents for 20 metals, such as Ca^{++} and Fe^{+++} .

The disclosures of the foregoing are incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

The present invention is directed to compounds of amine and quaternary ammonium salt derivatives of glycidyl ethers and glycidyl esters. The derivatives are preferably alkoxylated. These compounds can be prepared by reacting alcohols, alcohol alkoxylates, 5 fatty acids, or fatty acid alkoxylates with epichlorohydrin under acidic or basic conditions to produce alkyl glycidyl ethers or glycidyl esters, which are then reacted with amines or amine alkoxylates to produce the desired products.

More specifically, the present invention is directed to a composition of matter comprising a compound of the structural formula:



15 wherein

R_1 is C_8 to C_{22} alkyl, C_8 to C_{22} alkenyl, C_8 to C_{22} ester alkyl, C_8 to C_{22} ester alkenyl, C_8 to C_{22} amido alkyl, or C_8 to C_{22} amido alkenyl;

Q is $C_pH_{2p}O$;

n is an integer of from 0 to 60;

20 p is an integer of from 2 to 4;

R_2 is hydrogen, alkyl or ester alkyl of from 1 to 22 carbon atoms, or Q_1 ;

Q_1 is $(C_pH_{2p}O)_{n1}H$;

R_3 is hydrogen, alkyl of from 1 to 22 carbon atoms, or Q_2 ;

0072-IS

Q₂ is (C_pH_{2p}O)_{n2}H;

R₄ is hydrogen, alkyl of from 1 to 22 carbon atoms, or Q₃;

Q₃ is (C_pH_{2p}O)_{n3}H;

R₅ is hydrogen, alkyl of from 1 to 22 carbon atoms, oxygen, betaine, amido amine, polyamine,
5 polyamine alkoxylate, fatty amine, or Q₄;

Q₄ is (C_pH_{2p}O)_{n4}H;

n1, n2, n3, and n4 are independently selected from the group consisting of integers of from 1
to 60;

X is a counterion selected from the group consisting of species generated from mineral or
10 organic acids;

m is 0 or 1; and

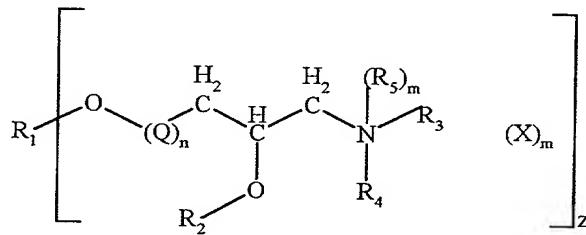
z is 1 to 4.

In another embodiment, the present invention is directed to a method of making a
compound of structural formula I comprising reacting a first compound selected from the
15 group consisting of alcohols, alcohol alkoxylates, amidoalcohols, amidoalcohol alkoxylates,
amidoamines, amidoamine alkoxylates, fatty acids, fatty acid alkoxylates, and mixtures thereof
with epichlorohydrin under acidic or basic conditions to produce a glycidyl ether or a glycidyl
ester; then reacting the glycidyl ether or glycidyl ester with a second compound selected from
the group consisting of amines, amidoamines, amidoamine alkoxylates, and amine alkoxylates
20 to produce a desired compound.

In still another embodiment, the present invention is directed to an article of
manufacture comprising a compound of structural formula I.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a first compound selected from the group consisting of alcohols, alcohol alkoxylates, amidoalcohols, amidoalcohol alkoxylates, amidoamines, amidoamine alkoxylates, fatty acids, fatty acid alkoxylates, and mixtures thereof is reacted with epichlorohydrin under acidic or basic conditions to produce a glycidyl ether or a glycidyl ester. The glycidyl ether or glycidyl ester is then reacted with a second compound selected from the group consisting of amines, amidoamines, amidoamine alkoxylates, and amine alkoxylates to produce a third compound. This third compound has the structural formula:



15 wherein

R_1 is C_8 to C_{22} alkyl, C_8 to C_{22} alkenyl, C_8 to C_{22} ester alkyl, C_8 to C_{22} ester alkenyl, C_8 to C_{22} amido alkyl, or C_8 to C_{22} amido alkenyl;

Q is $C_pH_{2p}O$;

n is an integer of from 0 to 60;

20 p is an integer of from 2 to 4;

R_2 is hydrogen, alkyl or ester alkyl of from 1 to 22 carbon atoms, or Q_1 ;

Q_1 is $(C_pH_{2p}O)_nH$;

R_3 is hydrogen, alkyl of from 1 to 22 carbon atoms, or Q_2 ;

0072-IS

Q₂ is (C_pH_{2p}O)_{n2}H;

R₄ is hydrogen, alkyl of from 1 to 22 carbon atoms, or Q₃;

Q₃ is (C_pH_{2p}O)_{n3}H;

R₅ is hydrogen, alkyl of from 1 to 22 carbon atoms, oxygen, betaine, amido amine, polyamine,
5 polyamine alkoxylate, fatty amine, or Q₄;

Q₄ is (C_pH_{2p}O)_{n4}H;

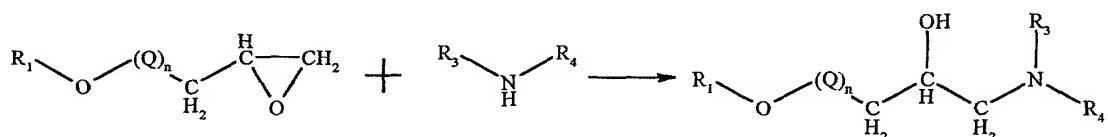
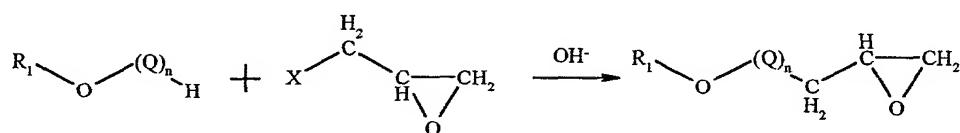
n1, n2, n3, and n4 are independently selected from the group consisting of integers of from 1
to 60;

X is a counterion selected from the group consisting of species generated from mineral or
10 organic acids;

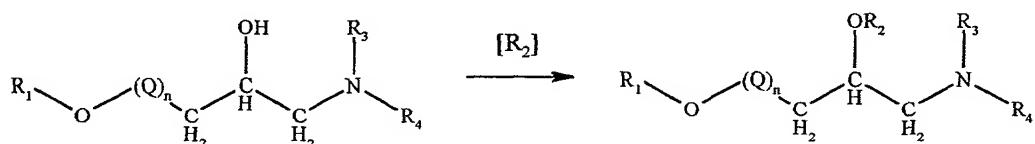
m is 0 or 1; and

z is 1 to 4.

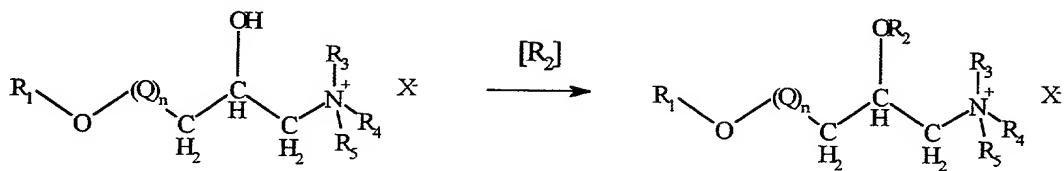
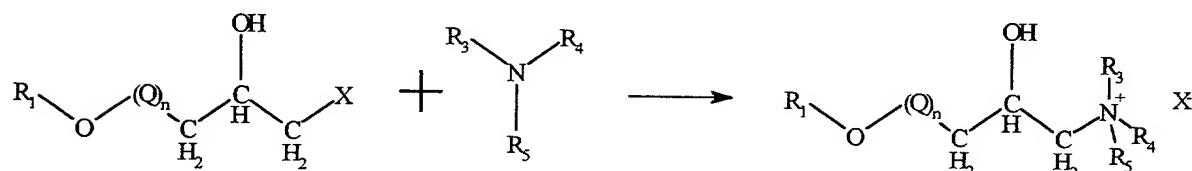
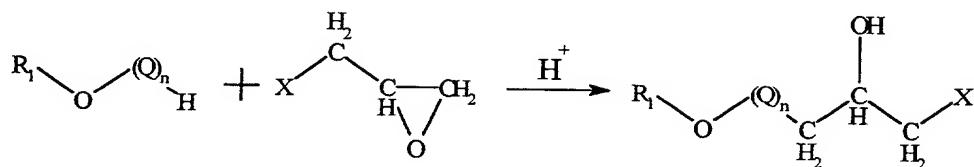
The amines of the present invention can be prepared according to the following general
equations, using, for convenience, the case where z in structural formula I is equal to 1:



20

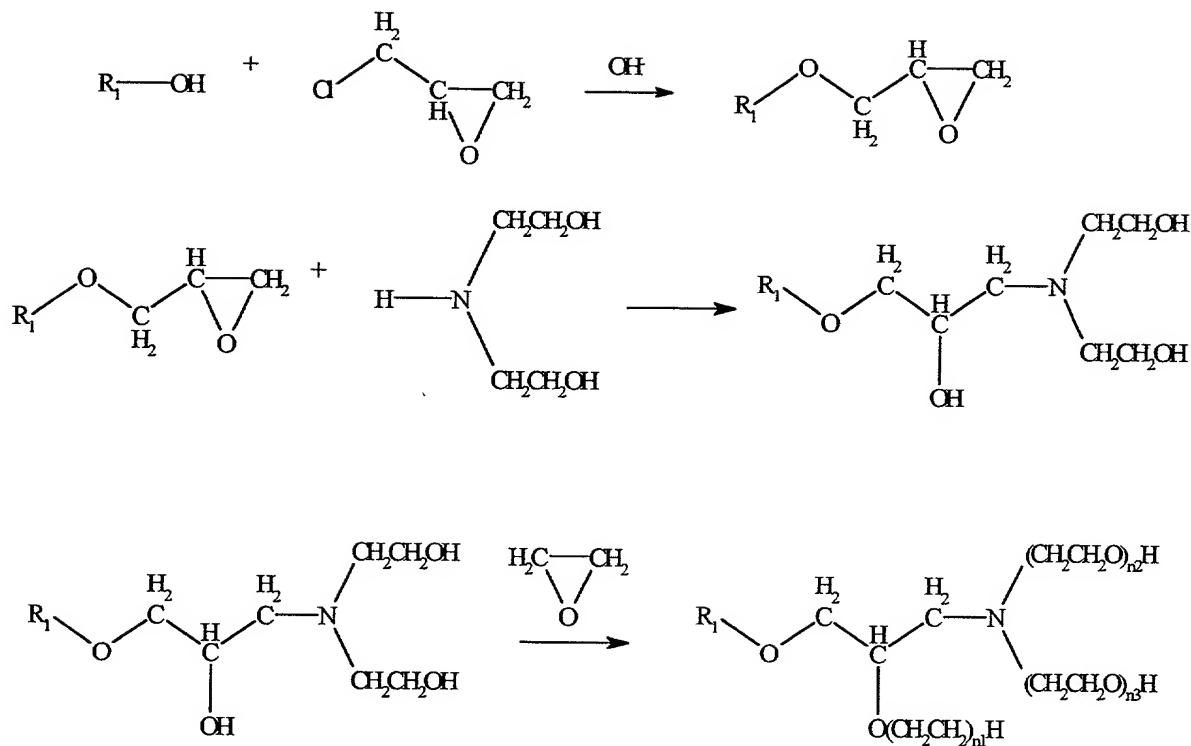


The quaternary ammonium salts of the present invention can be prepared according to the following general equations:



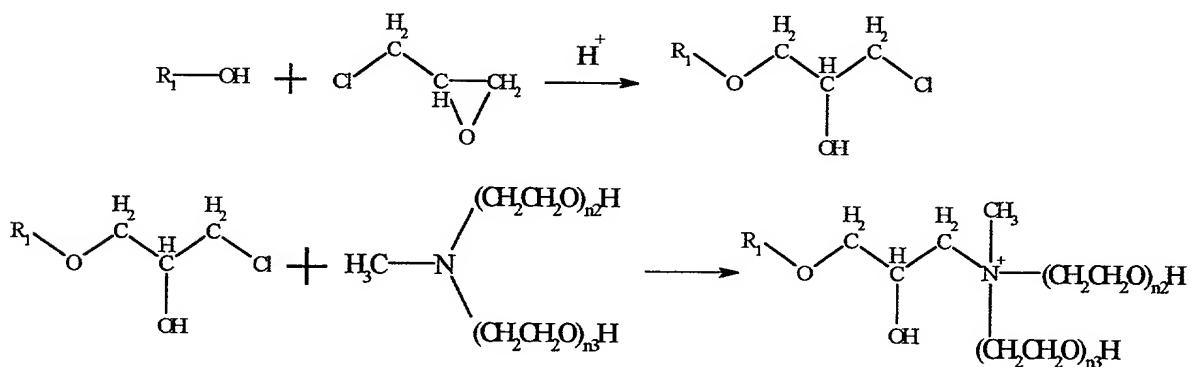
In a preferred embodiment of the present invention, ethoxylated amines of glycidyl

5 ethers are prepared by first reacting a fatty alcohol with epichlorohydrin under basic conditions to obtain glycidyl ethers, which are then reacted with diethanolamine and then further reacted with ethylene oxide. This reaction process can be represented as follows:



In another preferred embodiment of the present invention, ethoxylated amines of glycidyl ethers are prepared by first reacting a fatty alcohol with epichlorohydrin under acidic conditions to obtain glycidyl ethers, which are then reacted with ethoxylated methyl ethanolamine. This reaction process can be represented as follows:

5



Various features and aspects of the present invention are illustrated further in the examples that follow. While these examples are presented to show one skilled in the art how to operate within the scope of the invention, they are not intended in any way to serve as a limitation upon the scope of the invention.

5

EXAMPLES

Example 1 C₁₂ Glycidyl Ether

A 2 liter flask was charged with 392.0 g of Exxal-12 (a C₁₂ alcohol) and 1.0 g of tetrabutylammonium chloride (TBAC). To this solution was added 101 g of NaOH (97%) and 50 g of heptanes with good agitation. A dispersion was formed. Then dispersion was heated to 50° C, and 224 g of epichlorohydrin was added dropwise, so as to control the reaction temperature below 75° C. After the epichlorohydrin addition was completed, the reaction was continued for about 2-3.0 hours at about 65° C to complete the reaction. The reaction was monitored by gas chromatography. The salt thus formed was removed by filtration and the filtrates were condensed to give the desired Exxal-12 glycidyl ether. The structure was identified by IR and NMR, and its purity was examined by gas chromatography (GC).

Example 2

N,N-dihydroxyethyl-2-hydroxyl-3-alkyl(C₁₂)-oxy-propylamine

20

A quantity of 472.6 g of the Exxal-12 glycidyl ether prepared in Example 1 was charged to a one liter flask, and 167.8 g of diethanolamine was carefully added at 70° C. An exotherm was observed and the temperature was controlled below 100° C. After the reaction was under control, it was continued for about 2 hours at 90° C. The reaction was monitored by GC and the structure of the compound was confirmed by IR, and NMR.

Example 3

N,N-dihydroxyethyl-2-hydroxyl-3-alkyl(C₁₂)-oxy-propylamine ethoxylates

An autoclave was charged with 200 g of the N,N-dihydroxyethyl-2-hydroxyl-3-Exxal-

oxy-propylamine prepared in Example 2 and 1.0 g of KOH (45 % solution). After
5 dehydration, ethylene oxide was introduced to the reactor to react with N,N-dihydroxyethyl-2-
hydroxyl-3-Exxal-oxy-propylamine at 140° C. After the addition of the required amount of
ethylene oxide was completed, the reaction mixture was digested at about 140-150° C for
about 30 minutes to yield the product, an ethoxylated amine of C₁₂ glycidyl ether.

Example 4

1-Alkyl(C₁₂)-oxymethyl ethylenehydrin

A quantity of 115.3 g of epichlorohydrin was added to 187.6 g Exxal-12 in the
presence of 0.38 g of a BF₃ acetic acid complex and the reaction temperature was controlled
below 82° C. After the addition, the reaction was continued at 75° C for about 3.0 hours.
The progress of the reaction was monitored by GC and the chlorine content of the product
was determined by titration.

Example 5

Ethoxylated Quaternary Ammonium Salt of C₁₂ Glycidyl Ester

A mixture of the 100 g of the 1-alkyl (C₁₂)-oxymethyl ethylenehydride prepared in Example 4 (chlorine content = 14.6 %) and 285.8 g of methanolamine ethoxylate (EO=1.5) 5 was stirred in the presence of 2.0 g potassium carbonate at 110° C for about 12 hours to yield the surfactant, an ethoxylated quaternary ammonium salt of C₁₂ glycidyl ester.

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection afforded the invention.